Transition states of charge-transfer reactions: Femtosecond dynamics and the concept of harpooning in the bimolecular reaction of benzene with iodine

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Transition states of charge-transfer reactions: Femtosecond dynamics and the concept of harpooning in the bimolecular reaction of benzene with iodine

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We describe an approach for real-time studies of the transition-state dynamics of charge-transfer reactions. An application to the bimolecular reaction of benzene with iodine is reported. The measured 750 ± 50 fs transient growth of the free I atom product elucidates the nature of the transition state and the mechanism for the dissociative charge-transfer reaction. The mechanism is formulated in relation to the impact geometry and the dative bonding, which are crucial to condense-phase and surface reactions, and is supported by molecular dynamics. © *1995 American Institute of Physics.*

I. INTRODUCTION

Charge-transfer reactions are central to studies of dynamics of elementary chemical processes[1] and are ubiquitous in many areas of chemistry.[2] The transition state for A+BC systems has unique characteristics in charge-transfer (CT) reactions and represents a hybrid of covalent and ionic structures with an ultrafast interconversion (less than a picosecond), accompanied with bond breakage and bond formation. This process of "harpooning," $A^+\cdots B^-$–C, introduced by Michael Polanyi, has signature in the reactive scattering cross section,[1] in the absorption spectra of the A···BC species,[3,4] and in the femtosecond (fs) dynamics of the motion.[5] The Polanyi system, $Na\cdots XCH_3$,[6] is one in which many of these features are amenable to direct study in the transition-state region, as discussed below.

In this contribution, we report on a novel approach which makes it possible to directly study the transition-state dynamics of CT reactions. The entire system is prepared on a reactive potential energy surface and in a well-defined impact geometry. To define the zero of time, we start from the van der Waals (vdW) configuration in a molecular beam, similar to other real-time studies.[7] A fs pulse induces the CT. We then follow the dynamics of the transition state using probe pulses which monitor the transition state or the final products of the reaction using mass spectrometry. The system of interest here is the bimolecular reaction of benzene (Bz) with iodine:

$$\underset{\text{(reactants)}}{Bz\cdots I\text{–}I} \rightarrow \underset{\text{(transition state)}}{[Bz^+\cdots I^-\cdots I]^{\ddagger}} \rightarrow \underset{\text{(products)}}{Bz^+\cdot I^- + I}\ .$$

The system, as illustrated in Fig. 1, is rich in many aspects of the structure and dynamics, and has historic roots for nearly 50 years since the seminal works by Hildebrand[8] and Mulliken.[9]

The concept of the experiment is illustrated in Fig. 1 by considering two nuclear coordinates, the Bz–I and I–I distances. If the $t=0$ pulse ($\lambda^{\ddagger}$) is at the vdW distance, then the transition state is reached by direct CT, for a given geometry, followed by bond breakage along the I–I coordinate. On the other hand, if the $t=0$ pulse (λ^{∞}) is tuned to longer distances, then the situation is equivalent to a bimolecular collision with full impact parameters sampling; in this case the crossing of covalent to the ionic curve is crucial to the outcome. As shown in Fig. 1, vertical excitation from the vdW geometry to the CT state induces a fs electron jump from benzene to iodine and suddenly turns on the Coulomb field between the two. The iodine molecular anion is then rapidly pulled in by the strong electrostatic force to a closer distance from the benzene cation, and then the reaction occurs. The products are a free iodine atom and a $Bz^+\cdot I^-$ complex. By monitoring the appearance of the free I atom product, we are able to measure, for the first time, how fast a harpoon reaction takes place, in this case, 750 ± 50 fs.

The comparison with other (time-integrated) approaches is relevant. In Polanyi's experiments,[6] they reach the covalent branch and then by crossing, through harpooning, the final products are made. The scheme in Fig. 1 is identical to that of the $M+X_2$ harpoon reactions,[10] where M=alkali-metal atom and X=halogen atom, except that the present system requires a photon to induce the electron jump and enters the transition-state region directly. The preparation is from "beneath" the potentials of interest and in this regard analogous to Neumark's photodetachment experiments.[11] The preparation is off-resonant with the absorption of either reactants, similar in design to Brooks and Curl experiments.[12] The mechanism also bears a close similarity to that in reactions of $Xe\cdot X_2$ (Ref. 13) (X=Cl, Br) and $Hg\cdot Cl_2$ (Ref. 3) complexes reported by Jouvet and Soep, and the laser-assisted reactions of Xe/X_2 collision pairs reported by Setser's group;[4] the vdW complexes (or collision pairs) were excited to their CT states, by one or two photons, and the product (XeX* and HgCl*) emission was detected. Finally, unlike the hot-atom reactions,[7] the $Bz\cdot I_2$ system is entirely prepared on a reactive potential at $t=0$ and has a well-defined impact geometry, as discussed below.

II. EXPERIMENT

The experiments were carried out in a molecular beam apparatus interfaced with a fs laser system.[14] The $Bz\cdot I_2$ complex was produced by expanding a gas mixture containing benzene, iodine, and He through a pulsed valve. The molecular beam was skimmed and intersected by the fs laser pulses in the acceleration region of a linear TOF-MS.

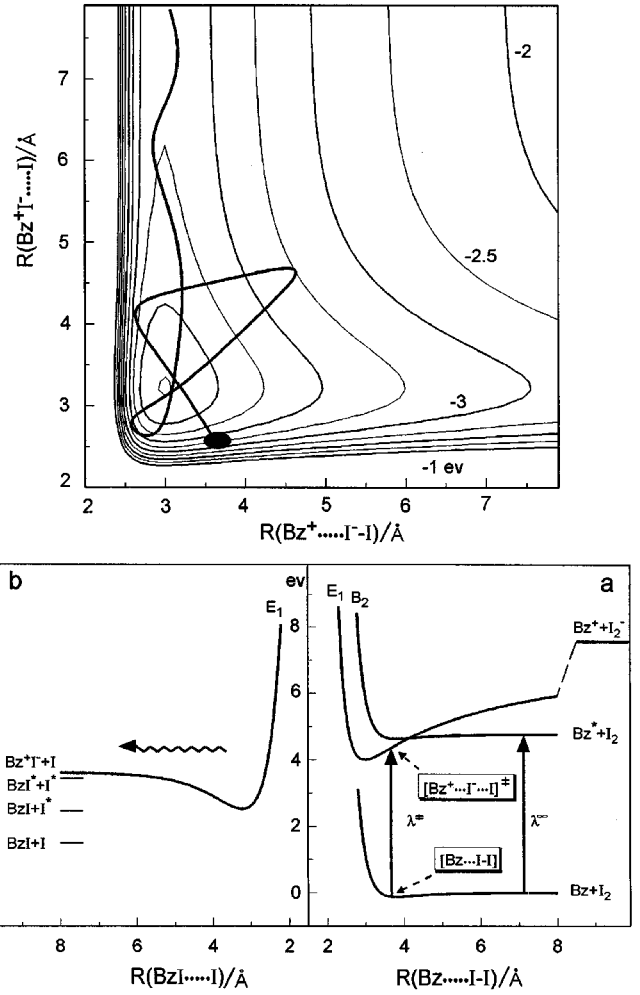

FIG. 1. Upper panel: A contour PES map of the CT reaction. The surface was constructed from a Morse potential for I_2^- (Ref. 27) plus a potential for $Bz^+ \cdot I^-$, the latter was deduced by adding the Coulombic attraction and a R^{-12} repulsion term to produce an ionic potential with $R_e = 3$ Å. The trajectory shown here takes 820 fs to proceed from the initial configuration ($R_{Bz-I} = 3.6$ Å, $R_{BzI-I} = 2.6$ Å) to the product with a separation of 8 Å in the I–I coordinate. Lower panel: Cuts along the reaction coordinate showing the entrance channel (a) and the exit channel (b) of the reaction.

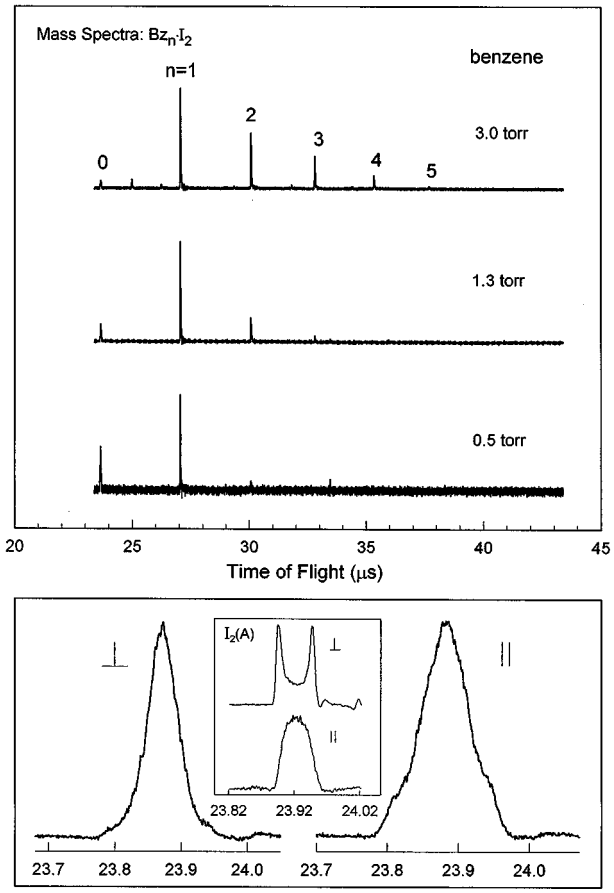

FIG. 2. Upper panel: TOF mass spectra for three benzene vapor concentrations with room temperature I_2 vapor and 800 torr of He. All spectra are normalized to the 1:1 $(Bz \cdot I_2)^+$ peak for clarity. Note that these ions are produced by a 1+1 REMPI process, as all clusters have strong CT absorption in this wavelength region and the two-photon energy (~9.0 eV) lies just above their ionization potentials. Therefore, the size distribution should closely reflect the true beam composition, and this is further supported by the temporal response described in the text. Lower panel: Iodine-atom TOF distributions for two pump-laser polarizations, perpendicular (left) and parallel (right) to the TOF axis (the TOF times are different in the two panels because of the acceleration voltages). For comparison, the insert shows TOF distributions of I atoms from the dissociation of I_2 (A) state (at 690 nm) through its perpendicularly polarized $X \rightarrow A$ transition; the splitting gives ~850 cm^{-1} of translational energy for the I atom.

The fs pump-laser pulses (275 nm) initiate the reaction and define $t=0$. The probe pulses (304.7 nm) then detect the free iodine atoms through a 2+1 REMPI (resonantly enhanced multiphoton ionization) process. Transient I atom growth was measured by monitoring the I^+ as a function of the pump-probe delay. The observed rise (~1.5 ps) is much slower than the cross correlation (650 fs), obtained *in situ* in the molecular beam. Figure 2 shows the mass spectra obtained for three different benzene vapor concentrations using the 275 nm laser alone. Clearly, at 0.5 torr of benzene only the 1:1 complex mass is present.

III. RESULTS AND DISCUSSION

For over a century, $Bz \cdot I_2$ and other related molecular complexes have been the focus of a great number of studies.[8,9,15] Benesi and Hildebrand[8] first reported UV absorption bands that are characteristic of iodine dissolved in aromatic hydrocarbon solvents, but could not be ascribed to either the aromatic or the iodine molecules alone. In the case of Bz/I_2 solution, the absorption maximum of this band is at 297 nm.[8] Gas phase studies of Bz/I_2 vapor mixtures also revealed a similar absorption band with the maximum shifted to 268 nm.[16]

Mulliken[9] attributed this strong absorption band to the excitation of the ground-state complex to the CT state with the aromatic molecule acting as the electron donor and the iodine as the acceptor, i.e., $Bz^+ \cdot I_2^-$. Several spectroscopic[17] and theoretical studies[18] have predicted that the $Bz \cdot I_2$ ground state has a C_{6v}, axial structure with the I–I bond being perpendicular to the benzene molecular plane. The heat of formation of this complex in the gas phase was determined by spectrometric methods to be on the order of 2–3 kcal/mol.[16,19]

In solution[20] and gas phases,[21] early studies have reported the formation of the benzene–iodine atom complex $(Bz \cdot I)$ after flash photolysis of Bz/I_2 mixtures. CT absorption

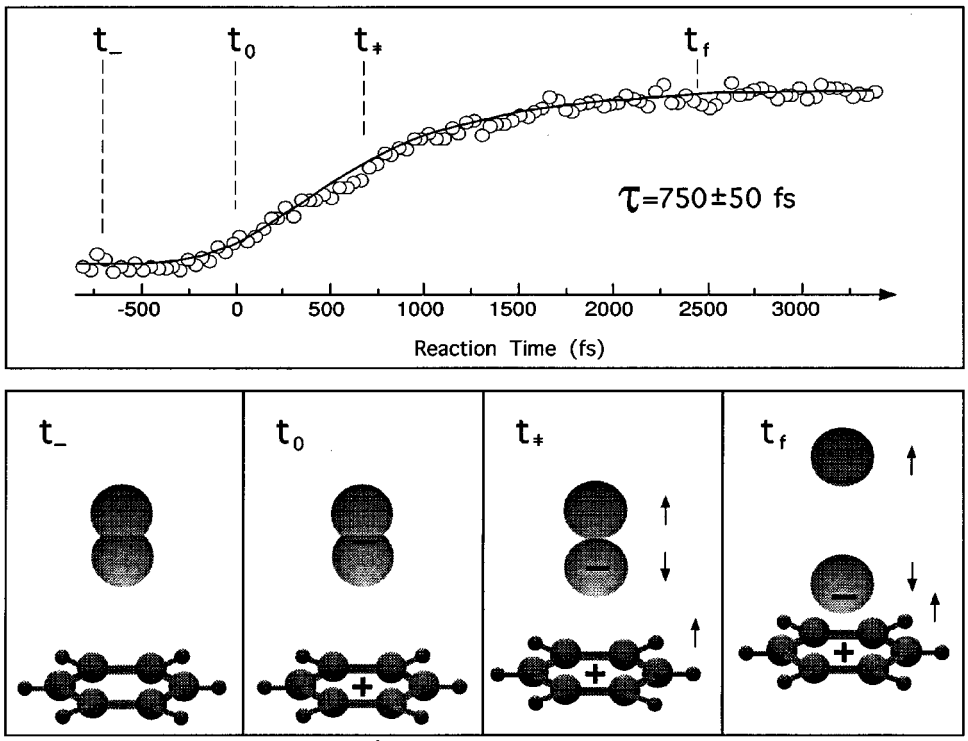

FIG. 3. fs transient of free iodine atoms (open circles) following the $Bz\cdot I_2$ complex excitation to its CT state by the 275 nm fs ($t=0$) laser pulse under the 1:1 complex condition (0.5 torr Bz). A single exponential fit (solid line) to this data with a response function convolution gives a rise time of 750 ± 50 fs. We have also performed a much longer scan and found that the I atom signal stays constant for at least 200 ps for the condition of the 1:1 $Bz\cdot I_2$. The four panels at the bottom describe the structural changes of the axial geometry, illustrating the complex before $t=0$ (t_-), at $t=0$ (t_0), in the harpoon region of the PES ($t_\ddagger$), and following the final breakage to $Bz^+\cdot I^-$ and I products (t_f).

of $Bz\cdot I$ was also observed at 430 nm in the gas phase[21] and at 480 nm in Ar matrix.[22] With ps and fs resolution, studies in solutions have elucidated the ultrafast time scale for their absorption,[23,24] and we shall address this issue of solvation elsewhere.[25]

For our molecular-beam fs studies, Fig. 3 displays the transient growth of free I atoms after the reaction is initiated by the $t=0$ pulse. The temporal behavior can be well simulated with a single exponential rise of 750 ± 50 fs. The transient I atom growth is observed only when benzene and iodine vapors are both present in the gas mixtures. When pure iodine vapor is expanded with He gas alone, we did not observe the characteristic temporal behavior of the 1:1 complex; instead, a very small (a factor of 10 or less) iodine transient (direct dissociation) due to the very weak absorption continuum of I_2 in this wavelength region.[26]

The CT band of the $Bz\cdot I_2$ complex is known for its strong absorption owing to the inherent charge-transfer nature of the transition as predicted by Mulliken's theory. Gas phase studies[16] have shown that the extinction coefficient of the $Bz\cdot I_2$ complex is about 150 times larger than that of the free I_2 in this wavelength region. This strong CT absorption explains why much more I atoms are produced from the $Bz\cdot I_2$ complexes even though their concentration is expected to be a few percent of I_2 in the molecular beam. The pump-laser photon energy employed here is about 1700 cm^{-1} lower than that of the free benzene $S_1\leftarrow S_0$ band origin; spectral shifts for this transition are usually smaller than ±200 cm^{-1} for many mixed bimolecular vdW complexes containing benzene. This choice again confirms the CT preparation.

The charge-transfer nature of the initially prepared state and the observed subpicosecond dynamics indicate that the reaction proceeds through the harpoon mechanism. The product we monitor is the I atom. The other product is the charge-transfer excimer $Bz^+\cdot I^-$, which might relax to its weakly bound ground state through either radiative or nonradiative processes and then dissociate; these processes are nanosecond-type. Based on the reported CT transition energy of the $Bz\cdot I$ complex,[21,22] we estimate that the zero-point of the product $Bz^+\cdot I^-$ lies at the most 2.5 eV above its ground state. This value places a lower limit of $\sim$0.5 eV of available energy for the reaction.

The observed fs dynamics of this dissociative CT reaction is related to the nature of bonding. Upon excitation to the CT state, an electron in the HOMO of benzene (π) is promoted to the LUMO of I_2 (σ^*). The molecular iodine anion ($D_0=1.1$ eV) is more weakly bound than the neutral ($D_0=1.58$ eV) due to the reduced bond order (electron in σ^*). Vertical electron attachment of ground state I_2 is expected to produce molecular iodine anions in some high vibrational levels below the dissociation limit.[27] In other words, after the electron transfer, the I–I bond is weakened but not yet broken. While vibrating, the entire I_2^- and benzene cation begin an excursion motion within the Coulombic field and the system proceeds from the transition-state region to final products. The observed 750 fs reaction time indicates that the transition state lives for a few vibrational periods before it breaks up to form the products. This is an important conclusion pertinent to dissociative CT reactions in solutions,[28] to CT surface reactions,[29] and to future transition-state studies of surface-aligned, photoinduced reactions.[30]

To give more insight into the molecular dynamics in the transition-state region, we performed preliminary classical trajectory calculations based on an empirical potential energy surface (PES) of the axial structure. A calculated PES along with a typical trajectory is shown in Fig. 1. Benzene was treated as a point mass with no internal degrees of freedom.

This approximation is justified by the fact that on the whole the internal vibrational motions of the benzene ring is well separated from the intermolecular motion by a large energy mismatch and that the reaction time is too short for these couplings to be effective. The classical trajectory calculations on this PES do produce reaction time scales consistent with the experimental results. As shown in Fig. 1, the transition state executes several vibrations before the I atom separates far enough to be detected as a free atom. The wave packet starts at a well-defined separation in the two coordinates, defining the impact geometry more clearly than in other studies of hot-atom reactions. In this regard, it is a (Bz) surface-aligned reaction.[29,30]

We have also examined the velocity profile in the exit channel to determine the translation energy released and the involvement of other possible reaction channels. These channels are depicted in Fig. 1 as final products. Isoenergetic with the initially prepared CT state ($\sim$4.5 eV), there are several repulsive states of I_2 that dissociate into I or I* due to ($\sigma \rightarrow \sigma^*$), ($\pi \rightarrow \sigma^*$), and two-electron ($\pi^* \rightarrow \sigma^*$) excitations.[26] The CT state of the $Bz \cdot I_2$ complex could, in principle, cross over to these repulsive surfaces through a ''back electron-transfer'' predissociation, e.g., $\sigma(I_2^-) \rightarrow \pi(Bz^+)$. These processes would put the system on purely repulsive surfaces which yield, e.g., Bz·I+I. The available energies, respectively, are 3.0 eV (I+I), 2.08 eV (I*+I) and 1.14 eV (I*+I*). Since Bz·I is very weakly bound ($\sim$0.1 eV at most), these channels should produce free I atoms with significant amount of translational energies that can be observed in the I^+ TOF (time of flight) distribution, as described in our previous publications.[31]

However, the observed I^+ TOF distributions do not show significant splitting or broadening (see Fig. 2) when the pump-laser polarization is either parallel or perpendicular to the TOF-MS axis. In fact, the observed TOF distribution is indicative of a broad translational energy distribution peaked at nearly zero. These observations suggest that the translational energy disposal is low and that the above discussed channels do not play a significant role. The reaction mechanism is featured by the elementary harpoon process.

IV. CONCLUSION

The results presented here reveal that the transition state of CT reactions can be studied directly at well-defined impact geometries. The dissociative CT reaction of benzene with iodine occurs with an elementary harpoon mechanism, but its transition state executes few vibrational periods before it breaks into products. The time scales for the CT ($<$50 fs) and for the product (I) formation (750 fs) define the degree of concertedness important to CT reactions at electrodes,[28] and, as reported in a forthcoming publication,[25] are crucial to studies in condensed media.[2,23,24] So far we have studied the electron donors benzene, mesitylene, and cyclohexane (see Ref. 25) and the results are in accord with this general picture. We have also extended the detection to different regions of the PES, and details will be given in our full account. The approach promises other applications, including different reactions, solvation dynamics, and CT reactions on surfaces.

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